POLISHING PAD, POLISHING APPARATUS AND POLISHING METHOD USING THE SAME

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a metal polishing pad, and a polishing apparatus and a polishing method using the same. More specifically, the present invention relates to a polishing pad for polishing a metal film used in production of a semiconductor devices, and a polishing apparatus using this polishing pad, and a polishing method using this polishing apparatus.

Description of Related Art

Recently, various fine processing technologies are studied and investigated, for highly integration and enhanced abilities of LSI. Of them, chemical mechanical polishing (chemical mechanical polishing, hereinafter, may be abbreviated as CMP) is noticed. CMP is a technology combining a chemical action and a mechanical action between a polishing composition and a polishing subject, and is an essential technology particularly in flattening an interlayer insulation film in a multi-layer wiring formation process, forming a metal plug, and forming an embedded metal wiring. The embedded metal wiring is formed by forming a metal film on a substrate and polishing this film.

In conventional CMP of a metal film, it is general to conduct polishing while feeding a polishing slurry containing abrasive particles into between a polishing subject and a polishing pad. However, in this method, the surface of a metal film is scratched and roughened, abrasive are embedded in a metal film, and further, a slurry has to be discarded. Therefore, it is investigated to conduct CMP by a pad itself without using a polishing slurry. As the polishing pad used of CMP, a complex called non-woven fabric type composed of polyester fibbed and polyurethane resin, and a porous polyurethane, and the like are usually used.

For the purpose of improving polishing speed, simplifying waste liquid treatment, and the like, use of a urethane foamed body pad obtained by adding particles of an inorganic oxide such as silica, ceria, alumina and the like as an abrasive particle previously into a polishing pad is investigated, however, the polishing speed is not recognized as satisfactory, and the surface of a metal is scratched by an inorganic oxide particle and roughened.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a metal polishing pad which provides high polishing speed, suppresses scratch and etching on the polishing surface, can give an excellent processed surface, and scarcely produces waste

containing a polishing agent even after completion of polishing, a polishing apparatus and polishing method using the same.

The present inventors have intensively studied for solving the above-mentioned problems, and resultantly found that the object can be attained by using a metal polishing pad having a functional group which captures a metal ion, and have completed the present invention.

Namely, the present invention relates to a metal polishing pad having a functional group which captures a metal ion.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention will be illustrated in detail below.

The metal polishing pad of the present invention is characterized in that it has a structure having a functional group capturing a metal ion.

The functional group capturing a metal ion may be permissible if it contains a coordinate atom forming a complex with a metal, and specifically, functional groups containing at least one atom selected from the group consisting of an oxygen atom, nitrogen atom, sulfur atom, phosphorus atom, arsenic atom and selenium atom are listed.

Specific examples of the functional group coordinated with

an oxygen atom include -OH derived from alcohols, phenols or enols, -COOM (M represents hydrogen, alkali metal, alkali earth metal or ammonium group) derived from carboxylic acids or salts of carboxylic acids, >C=O derived from aldehydes, ketones or quinines, -O- derived from ethers, -COOR group (R represents a hydrocarbon group) derived from esters, $-CONH_2$ derived from amides, -NO group derived from nitroso compounds, $-NO_2$ derived from nitro compounds, $\equiv N-O$ derived from N-oxides, $-SO_3M$ (M has the same definition as described above) derived from sulfonic acids or salts of sulfonic acids, -PHO(OM) (M has the same definition as described above) derived from hypophosphorous acids or salts of hypophosphorus acids, $-PO(OM)_2$ (M has the same definition as described above) derived from phosphorus acids or salts of phosphorus acids, and $-AsO(OM)_2$ (M has the same definition as described above) derived from arsonic acids or salts of arsonic acids.

Examples of the functional group coordinated with a nitrogen atom include $-NH_2$ derived from primary amines, >NH derived from secondary amines, $\equiv N$ derived from tertiary amines, -N=N- derived from azo compounds and heterocyclic compounds, >C=N- derived from Schiff bases and heterocyclic compounds, $-CONH_2$ derived from amides, >C=N-OH derived from oximes, >C=NH derived from imines and enamines, -SCN derived from thiocyanates.

Examples of the functional group coordinated with a sulfur atom include -SH derived from thioalcohols and thiophenols, -S- derived from thioethers, >C=S derived from thioaldehydes and thioketones, -COSM (M has the same definition as described above) derived from thiocarboxylic acids or salts of thiocarboxylic acids, -CSSM (M has the same definition as described above) derived from dithiocarboxylic acids or salts of dithiocarboxylic acids, $-CSNH_2$ derived from thioamides, and -NCS derived from isothiocyanates.

Examples of the functional group coordinated with a phosphorus atom include >P- derived from primary, secondary, tertiary alkyls and arylphosphines.

Examples of the functional group coordinated with an arsenic atom include >As- derived from primary, secondary, tertiary alkyls and arylarsenes.

Examples of the functional group coordinated with a selenium atom include -SeH derived from selenols, >C=Se derived from selenocarbonyl compounds, -CSeSeM (M has the same definition as described above) derived from diselenocarboxylic acids or salts of diselenocarboxylic acids.

Among these functional groups capturing a metal ion, -OH, -COOM, >C=O, -O-, $-SO_3M$, $-PO(OM)_2$, $-NH_2$, >NH, $\equiv N-O$, -SH, -S-, -COSM, -CSSM are preferable (M has the same definition as

described above).

These functional groups may be present alone or in combination of two or more. As the polishing pad having two or more functional groups, for example, those having functional groups derived from aminocarboxylic acids, amino alcohols, amino phosphonic acids are listed.

It is preferable that the functional group capturing a metal ion exists on the surface of a polishing pad, however, the functional group may also exist in a polishing pad since the same effect is obtained if the functional group is exposed to the surface of a polishing pad by a stress in polishing and contacts with a polishing subject, or if the functional group is exposed to the surface of a polishing pad by toothing the surface of a polishing pad using a dresser and the like fixed to an abrasion grain such as diamond and the like, and contacts with a polishing subject.

As the polishing pad having a functional group capturing a metal ion, ion exchange resins or ion exchange fiber can be used. The ion exchange resins means a synthetic resin having an anionic group or cationic group which can be ion-changed, and having mainly a form of a particle, and the ion exchange fiber means a resin in the form of fiber endowed with the same

ion exchange ability as that of an ion exchange resin.

As the ion exchange resin, cation exchange resins, anion exchange resins and chelate resins are listed.

As the cation exchange resin, for example, cation ion exchange resins having $-SO_3M$ (M has the same definition as described above) derived from sulfonic acids or salts of sulfonic acids and -COOM (M has the same definition as described above) derived from carboxylic acids or salts of carboxylic acids, as a functional group, and containing a styrene-divinylbenzene copolymer and the like as a substrate are listed.

As the anion exchange resin, for example, anion exchange resins having an amino group, mono-substituted amino group, di-substituted amino group and the like, as a functional group, and containing a styrene-divinylbenzene copolymer and the like as a substrate are listed.

As the chelate resin, those having an aminocarboxylic acid, aminophosphonic acid, imino diacetic acid and the like, as a functional group, and containing the substrate as that of the ion exchange resin are listed.

As the ion exchange fiber, cation exchange fiber, anion exchange fiber and chelate fiber are listed like the ion exchange resin.

As the cation exchange resin, for example, cation ion

exchange resins having -SO_3M (M has the same definition as described above) derived from sulfonic acids or salts of sulfonic acids and -COOM (M has the same definition as described above) derived from carboxylic acids or salts of carboxylic acids, as a functional group, and containing polyvinyl alcohol and the like as a substrate are listed.

As the anion exchange resin, for example, anion exchange resins having an amino group, mono-substituted amino group, di-substituted amino group and the like, as a functional group, and containing polyvinyl alcohol and the like as a substrate are listed.

As the chelate resin, those having an aminocarboxylic acid, aminophosphonic acid, imino diacetic acid and the like, as a functional group, and containing the substrate as that of the ion exchange fiber are listed.

As the polishing pad of the present invention, materials having a functional group capturing a metal ion, such as the above-described ion exchange resins and ion exchange fiber and the like can be processed into a sheet which is used.

Further, a resin having no functional group capturing a metal ion may be processed into a sheet to which then a functional group is introduced. Known methods can be used for introducing the functional group. For example, methods in which the surface of an olefin-based resin such as polyethylene, polypropylene

and the like, a polyurethane resin, a polyimide resin, epoxy resin, polysulfone resin and the like is irradiated with an ionizing radiation to introduce an ion exchange group (for example, radiation graft polymerization method), methods of introducing a functional group by immersing activated carbon fiber sheer or multifilament of long fiber, spun thread of short fiber, woven or knitted cloth thereof, unwoven cloth, fiber obtained by combining or mix-spinning two or more fibers, vegetable fibers such as cellulose fiber and the like, animal fibers such as cotton, wool and the like, into a drug solution, and other methods are listed. Further, a functional group may be introduced by addition reaction of a compound having a functional group in producing a polyurethane resin, polyimide resin, epoxy resin, polysulfone resin and the like, and the resulted resin may be processed into a sheet which is used as a pad.

A second sheet containing no functional group, and the like may also be laminated to the rear surface of a sheet of such an ion exchange resin and the like, for the purpose of reinforcing the mechanical strength of the sheet, complementing the elastic modulus of a pad necessary for polishing, and the like.

Of these ion exchange resins and ion exchange fiber having a functional group capturing a metal ion, the chelate resin

or chelate fiber is a resin or fiber having on the surface a polydentate ligand having a plurality of coordinating atoms forming a complex with a metal. In general, when a polydentate ligand having two or more coordinating atoms is bonded to a metal ion, a chelate ring is formed, and stability thereof increases higher that of a complex in which a unidentate ligand is coordinated, and consequently, an ability of capturing a metal ion, polishing subject increases, desirably.

The metal polishing pad of the present invention may be a pad containing a particle having a functional group capturing a metal ion. Specifically, pads are listed which are obtained by a method in which the above-mentioned ion exchange resin and ion exchange fiber is finely ground and the ground material is mixed with a binder polymer, and the mixture is subjected to thermal extrusion or cast molding using a solvent, to give a pad. The form of a particle having a functional group capturing a metal ion may be spherical or unstable form. The binder polymer is not particularly restricted providing it can be mixed with particles.

Next, the polishing apparatus of the present invention will be illustrated.

The polishing apparatus of the present invention is characterized in that it comprises an apparatus of allowing

a polishing subject having a metal surface to contact with a metal polishing pad having a functional group capturing a metal ion confronting the polishing subject, and applying pressure uniformly between them, an apparatus of rotating or transferring a polishing subject and a polishing pad while maintaining contact between them, and an apparatus of feeding a polish promoting agent for promoting polishing into between a polishing subject and a polishing pad.

The polishing subject having a metal surface is usually fixed to a polishing head, and the metal polishing pad having a functional group capturing a metal ion confronting the polishing subject is usually fixed to a polishing surface plate. The polishing subject and polishing pad are rotated or transferred while keeping the contact of them, and this rotation or transfer is usually effected by rotating or transferring a polishing head and polishing surface plate.

The polishing head for fixing a polishing subject having a metal surface is not particularly restricted, and various heads can be used.

The size of the polishing head may be allowable if the polishing head can fix a polishing subject, and this size may be larger or smaller than that of a surface plate for fixing the polishing pad.

As the method of fixing a polishing subject, methods of

utilizing adsorption by a vacuum pump, of pasting with an adhesive and the like, and of fixing by utilizing a spring and the like, are listed.

The surface plate for fixing a polishing pad is also not particularly restricted, and various plates can be used.

The size of the polishing surface plate may be allowable if the polishing surface plate can fix a polishing pad, and this size may be larger or smaller than that of a polishing head for fixing a polishing subject.

The form is also not particularly restricted, and may be in the form of disk, ellipse or rectangle, or a structure having a curved surface for fixing a polishing pad may also be adopted.

As the method of fixing a polishing pad, methods of utilizing adsorption by a vacuum pump, of pasting with an adhesive and the like, and of fixing by utilizing a spring and the like, are listed.

The polishing head and polishing surface plate are not particularly restricted providing they are in positional relation in which they confront each other, and a polishing head may be placed on the upper side of an apparatus and a polishing surface plate may be placed on the lower side of an apparatus, or inversely, a polishing surface plate may be placed on the upper side of an apparatus and a polishing head may be placed

on the lower side of an apparatus.

The size of a polishing pad is also not particularly restricted.

The polishing apparatus of the present invention preferably comprises a driving apparatus for allowing a polishing subject and a polishing pad to contact each other under a certain pressure and rotating or transferring both of or either one of them while keeping the contact, and a pressing apparatus for applying a pressure uniformly to the surfaces in contact condition. Effective polishing can be effected by using this apparatus and rotating and transferring a polishing subject and a polishing pad while keeping contact thereof under a constant pressure.

The driving apparatus and pressing apparatus for allowing a polishing subject and a polishing pad to contact each other are not particularly restricted, and a structure in which a polishing head moves toward and contacts with a polishing surface plate fixed and a pressure is applied thereon may be permissible, or a structure in which a polishing surface plate is allowed to contact with a polishing head fixed, inversely, and a pressure applied thereon may be permissible. A pressure after contact may be applied from the polishing head side, from a polishing surface plate, or from both of them.

The method of applying a pressure is also not restricted,

and methods of feeding air or a gas such as nitrogen and the like, and mechanical methods using a spring, oil pressure and the like, may be used.

The driving apparatus for rotating and transferring a polishing head and polishing surface plate is also not particularly restricted, and a plurality of driving apparatuses may be combined and rotation and transferring may be combined. Specifically, a driving apparatus of rotating a polishing head and a polishing surface plate separately, an apparatus of transferring a polishing head or a polishing surface plate toward left and right directions, an apparatus of rotating a polishing head or a polishing surface plate and further transferring both of them or either one of them toward left and right directions, or an apparatus of rotating a polishing head, and transferring a polishing surface plate toward left and right directions and toward to and fro, further, a driving apparatus which can freely move a polishing head, a driving apparatus in which a polishing surface plate is so placed that it moves like a belt conveyer between two rotation axes along the rotation direction of the axes, and other apparatuses are listed.

The polishing apparatus of the present invention has an apparatus of feeding a polish promoting agent for promoting polishing into between a polishing subject and a polishing pad

contacting each other.

The feeding apparatus usually comprises a vessel for keeping and storing a polish promoting agent, a pump of feeding a promoting agent from the vessel to a polishing surface, a gas feeding and controlling line for transporting with a gas and the like, and a promoting agent feeding piping. The material thereof is not particularly restricted providing it is not corroded by the action of a polish promoting agent. In the feeding piping, a filter for removing fine particles and the like in a promoting agent may be provided.

The position of a feeding port of a feeding piping is not particularly restricted providing a polish promoting agent can be fed into between a polishing subject and a polishing pad, and for example, a polish promoting agent may be fed on a pad by placing the port above the polishing pad place horizontally, or a polish promoting agent may be fed to the surface of a pad by providing a feeding piping penetrating a polishing surface plate and the polishing pad.

As the polish promoting agent for promoting polishing is not particularly restricted providing it contains an oxidizer.

As the oxidizer, known oxidizers can be applied, and for example, hydrogen peroxide, iodic acid, iodate and the like are listed, and hydrogen peroxide is preferably used.

The concentration of an oxidizer in a polish promoting agent

is preferably from about 0.1 to 15% by weight. When the concentration of the oxidizer is less than 0.1% by weight, an effect of improving polishing speed may not be manifested easily, and when over 15% by weight, improvement in polishing speed comparable to concentration may not be recognized, leading to diseconomy.

pH of a polish promoting agent is not constant since effective pH value differs depending on the kind of a functional group, and the kind of a polishing subject metal, and usually from about 1 to 8, preferably from 2 to 6. When pH of a polish promoting agent is less than 1, a problem of corrosion of a polishing apparatus and the like may occur. pH of the polish promoting agent of the present invention can be controlled by using a known acid and alkali. It is preferable to use acids and alkalis such as nitric acid, phosphoric acid, sulfuric acid, ammonium hydroxide, amine and the like, containing no metal ion.

The polish promoting agent may not substantially contain a solid abrasive particle or may contain a solid abrasive particle. Examples of the abrasive particle include abrasive particles of inorganic oxides such as silica, alumina, ceria, titania, zirconia and the like, and abrasive particles of organic materials such as polystyrene, polyacryl, polyvinyl chloride and the like.

Further, in the polish promoting agent, surfactants and

corrosion inhibiters such as benzotriazole and the like can be used, if necessary, as additives for improving surface properties of a polishing surface. As the surfactant, anionic, cationic, nonionic, and ampholytic surfactants can be used, and they can be used in combination of two or more.

Further, the polishing apparatus in the present invention preferably comprises a regenerating agent which regenerate a functional group deactivated by capturing a metal ion, and a functional group regeneration treatment apparatus which allows a polishing subject to contact with a polishing pad after polishing. Regeneration of a functional group means releasing of a metal ion from a functional group arrested a metal ion, and indicates recovering of an ability of a functional group of capturing a metal ion.

As the regenerating agent for regenerating a functional group de-activated, any of an acidic aqueous solution and an alkaline aqueous solution can be used depending of the kind of a functional group contained in a polishing pad.

The apparatus of regenerating a polishing pad by these regenerating agents is not particularly restricted providing it has a mechanism of allowing the polishing pad to contact with the regenerating agent. Specifically, those having a mechanism of blowing a regenerating agent to the surface of

a pad after completion of polishing, or those having a mechanism of immersing a pad in a regenerating agent solution, may be permissible. Particularly by conducting a regeneration treatment immediately on a pad directly after completion of polishing and by using subsequently a polishing treatment, polishing ability of a polishing pad is stabilized and polishing can be effected more efficiently.

The polishing pad and polishing apparatus of the present invention can be used for polishing of various metals, suitably copper-based metals. The polishing pad and polishing apparatus are preferably used for polishing of metals films, particularly, copper-based metal films formed on a semiconductor substrate. As the copper-based metal, a pure copper film, copper alloy film and the like are listed.

By using the polishing pad and polishing apparatus of the present invention, a metal can be polished at high speed, generation of scratch on the polishing surface can be suppressed, and etching of a metal can be suppressed.

The polishing method of the present invention is a method of polishing a metal by chemical mechanical polishing, and is characterized in that it uses the above-mentioned pad and apparatus of the present invention as a polishing pad and a

polishing apparatus, respectively. The polishing method of the present invention can be preferably applied to metal films, particularly, to metal films formed on a semiconductor substrate, of them, to a metal film.

EXAMPLES

The following example illustrate the present invention below but it is needless to say that the example does not limit the scope of the invention.

Example 1

Cloth made of chelate fiber obtained by introducing an imino diacetic acid group as a functional group into cellulose fiber was used as a polishing pad. This polishing pad was fixed to a polishing surface plate, and a circular copper plate fixed to a polishing head was polished by using a polishing machine (manufactured by PRESI, MECAPOL P-200). A polish promoting agent having a pH of 4 obtained by adding nitric acid to a 1.5 wt% hydrogen peroxide solution was prepared in a vessel, and the solution was fed to the surface of the pad by a pump. The polishing conditions included a rotation of a polishing surface plate of 100 rpm, a rotation of a polishing head of 75 rpm, a polishing pressure of 130 g/cm^2, a flow rate of a polish promoting agent of 100 ml/minutes, and a polishing time of 2 minutes. The copper plate had a polishing speed of 428 Å

/minute.

A copper plate was polished in the same manner as in example 1 except that a polyurethane resin-impregnated polyester non-woven fabric SUBA400 (trade name: manufactured by Rodel) was used instead of the pad having an imino diacetic acid group, as a polishing pad. The copper plate had a polishing speed of 34 Å/minute.

The polishing speed was very slow in Comparative Example 1 using non-woven fabric having no functional group capturing a metal ion as compared with Example 1 using clothe having an imino diacetic acid group as a polishing pad.

By using the metal polishing pad, polishing apparatus having this polishing pad, and the metal polishing method using them according to the present invention, metals, particularly, a metal film can be polished at high speed, occurrence of scratch on the polishing surface can be suppressed, etching on a metal can be suppressed, and a particularly excellent processed surface can be obtained, further, a waste containing inorganic abrasive grains and the like is scarcely produced after completion of polishing. Therefore, the pad, polishing apparatus and polishing method of the present invention manifest extremely large industrial values.